

**Flammability Testing of Fabrics Treated with Oil-Based
Shear Thickening Fluids**

by Paul Nenno, Wai Chin, and Eric D. Wetzel

ARL-TR-6936

May 2014

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**Paul Nenno, Wai Chin, and Eric D. Wetzel
Weapons and Materials Research Directorate, ARL**

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14. ABSTRACT Fabrics treated with paraffinic oil and a paraffinic oil-based shear thickening fluid (STF) are evaluated under flammability testing. The tested fabrics include a woven cotton-nylon blend, a woven Kevlar textile, and a hybrid ultrahigh molecular weight polyethylene (UHMWPE) – Kevlar felt. The oil-based STF is a colloid of silica nanoparticles in a paraffin oil. Test results show that the flammability of fabrics with oil addition is slightly increased, while the flammability of fabrics with STF addition was unchanged or slightly decreased. These results suggest that oil-based STFs could be used as fabric treatments, such as to enhance ballistic, puncture, or stab performance, without a significantly negative effect on flammability. Furthermore, concepts are presented for tailoring an STF to provide enhanced flammability resistance.				
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1. Introduction

Shear thickening fluids have been studied for various body armor and injury prevention applications. For body armor applications, polyethylene glycol and silica suspensions have been intercalated in Kevlar^{*} fabrics in order to enhance the ballistic performance (1, 2) or stab resistance (3). Shear thickening fluids (STFs) have been shown to increase the force needed to puncture fabrics with a hypodermic needle, with potential application to medical gloves or police search gloves (4). STFs have also been proposed in rate-dependent devices such as foam pads (5) or rate-dependent tethers (6).

Shear thickening fluids exhibit fluid-like properties at low deformation rates, but solid like properties at high deformation rates (7–10). These fluids are “non-Newtonian” as they exhibit a non-linear dependence on shear rate or shear stress so that viscosity increases with increasing shear rate or stress. Discontinuous shear thickening, a dramatic form of shear thickening, can occur in densely packed suspensions or colloids. Discontinuous STFs are relatively flowable at low stresses but can become very viscous or solid-like at high stresses.

Most published shear thickening fluids consist of a glycol polymer media, with dispersed silica particles (7–10). ARL has also developed shear thickening fluids based on paraffinic oil (6, 11). Paraffinic oil STFs offer a number of potential advantages over glycol-based STFs. Figure 1 compares the rheological response of a number of STF systems, including one based on silica particles in paraffinic oil. The paraffinic oil STF shows a higher critical shear rate, more discontinuous shear thickening response, and lower nominal viscosity than the glycol system (11). Furthermore, paraffinic oil-based systems appear to have longer colloidal stability compared to glycol and water-based STFs. Paraffinic oil STFs also are inherently hydrophobic, so that textiles treated with paraffinic oils will be water-repelling. However, a major concern with paraffinic oils is that they are, in bulk, flammable. Therefore, it is possible that a textile treated with paraffin oil STF would become flammable, an unacceptable characteristic for a body-worn textile such as for body armor or gloves.

The objective of this study is to investigate the flammability of shear thickening fluid treated Kevlar in order to determine the viability of using an oil-based carrier for shear thickening fluids used in body armor application. A secondary objective of this study will be to comparatively evaluate the flammability of other commonly used fabrics with and without shear thickening fluid treatment.

* Kevlar is a registered trademark of E.I. DuPont de Nemours and Company, Wilmington, DE.

To our knowledge this is the first study of the flammability of STFs or STF-containing materials. However, the use of silica-containing coatings as flame retardants is well-established (12, 13); therefore, it is reasonable to expect that a silica-containing STF might be effective as a flame retardant textile coating.

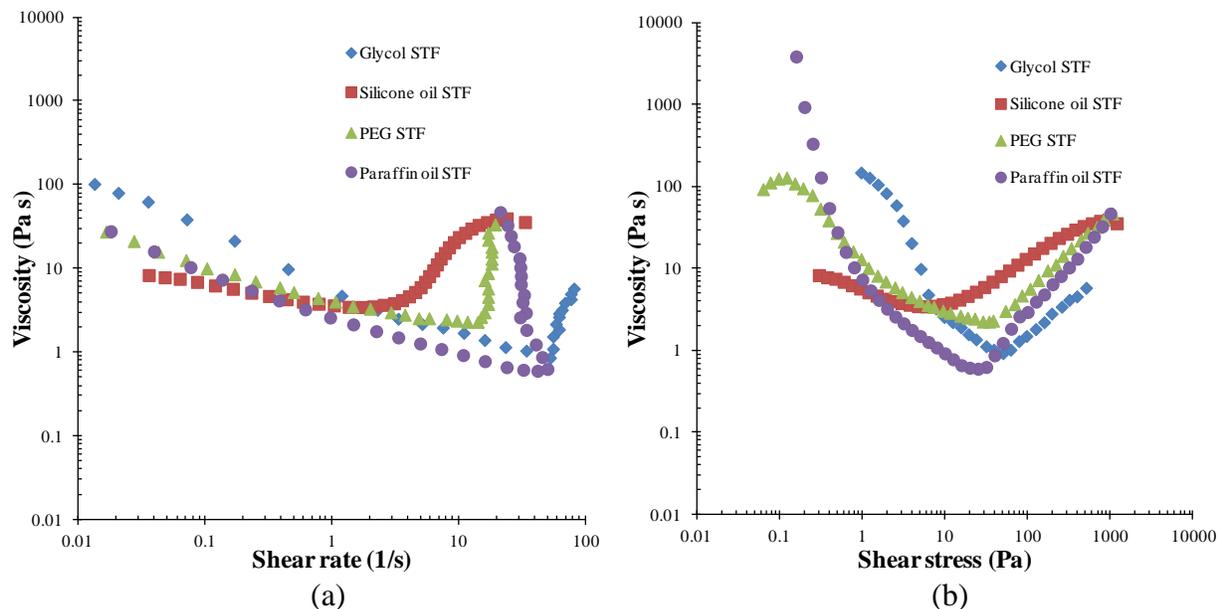


Figure 1. Effect of carrier fluid chemistry on suspension rheology. (a) Viscosity vs. shear rate, and (b) viscosity vs. shear stress.

Flame initiation, spread, and extinction are complex processes dependent upon a number of material and thermodynamic properties. Flammability is usually characterized through either a series of calorimetric measurements with sophisticated equipment, or through a relatively simple strip burning test. In such a test, a sample is exposed to a consistent flame and both the fabric's ignition and combustion resistance are quantified. Typical parameters measured through the strip test are afterflame time, afterglow time, and char length. The afterflame time refers to the time which a material burns after its ignition source is removed. Samples that immediately self-extinguish will have a low afterflame time. For materials that burn, a higher afterflame time can be indicative of a lower flame propagation rate, as it takes longer for the flame to travel along the full length of the sample. The afterglow time refers to the duration of time that the fabric glows after flaming has stopped. Generally, more flame resistant materials will show a shorter afterglow time. Finally, the char length indicates how much structural damage was done to the fabric through the process of testing. Materials with better flammability resistance have a shorter char length. Additional qualitative observations include relative intensity of flame, color of smoke, or presence of dripping. All of these characteristics can be taken into consideration when assessing the flammability behavior of fabrics via strip testing.

2. Experimental

2.1 Materials

2.1.1 Shear Thickening Fluids

STFs were formulated by dispersing 450-nm silica nanoparticles into a paraffinic oil (table 1). The volume fraction (ϕ) of particles in the colloid was determined using the known added masses of particle and fluid (m_{particle} , m_{fluid}), and particle and fluid densities (ρ_{particle} , ρ_{fluid}) according to

$$\phi = \frac{m_{\text{particle}} / \rho_{\text{particle}}}{m_{\text{particle}} / \rho_{\text{particle}} + m_{\text{fluid}} / \rho_{\text{fluid}}} \quad (1)$$

Particle dispersions were created by measuring out the required quantity of particles and oil into a 32-oz jar, then roll mixing in the jar for 24 h. After dispersion, suspensions were degassed for 2 h using a vacuum oven set at a temperature of 50 °C and a pressure of 1000 mTorr.

Table 1. Shear thickening fluid characteristics.

Sample name	Particle	Carrier fluid	Particle density (g/mL)	Fluid density (g/mL)	Volume fraction (vol particle/vol total)	Mass fraction (g particle/g total)
Oil-STF	450nm silica	Paraffin oil	2.05	0.86	0.533	0.732

2.1.2 Fabric

The shear thickening fluids were intercalated into style K706 plain-woven Kevlar fabric (600d KM2 yarns at 34 × 34 yarns per inch (in), areal density of 180 g/m²) from JPS Composites (Anderson, SC); Army Combat Uniform (ACU) ripstop woven NyCo fabric (50% cotton, 50% nylon with areal density 220 g/m²); and Armorfelt felted aramid / ultrahigh molecular weight polyethylene (UHMWPE) blend (250 g/m²). Note that, unlike currently fielded flame resistant ACUs, this ACU fabric is not intended to be flame resistant. Samples were cut into rectangles of 76 mm (3.0 in) × 300 mm (12 in) according to ASTM D6413. Five rectangles were prepared so that the long direction is in the direction of the warp yarns and five rectangles were prepared so that the long direction is in the direction of the fill yarns. A diagram of the two different sample orientations is shown in figure 2.

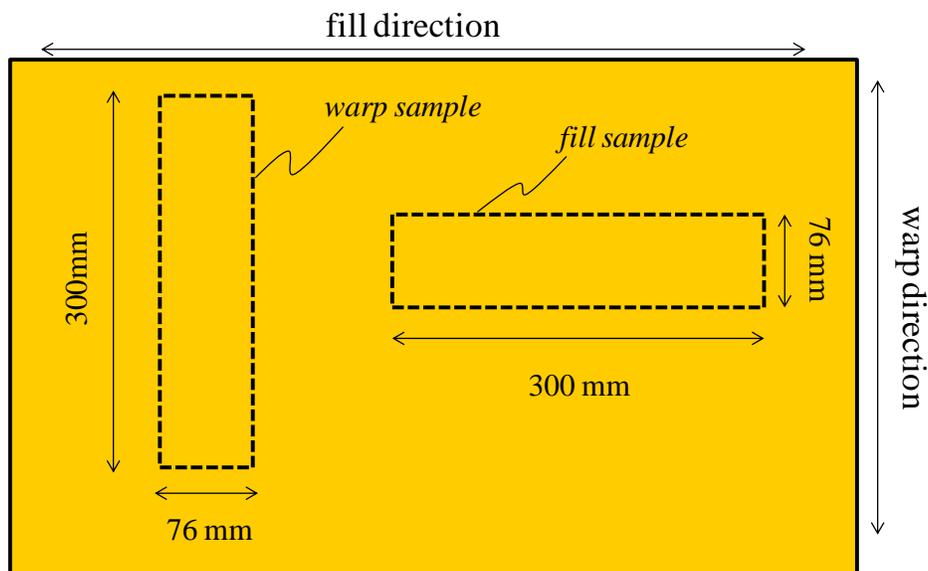


Figure 2. Schematic of sample orientations.

2.2 Methods

2.2.1 Fabric Preparation

Fabric was treated with shear thickening fluid by preparing a dip bath consisting of 3:1 volume ratio of hexane (ACS reagent 99.5% mix of isomers) to shear thickening fluid. The dip bath was prepared by diluting the STF and hexane in a 32-oz jar by stirring with a magnetic stir bar (450 rpm) for 4 h, followed by pouring the mixture into a shallow dip pan. Fabric was submerged in the bath for 30 s and then excess liquid was removed using a set of rollers. Fabrics were allowed to dry at standard room temperature and pressure for 48 h in a vertical fume hood (face velocity 99 fpm). A second dip bath was prepared consisting of 6.51:1 volume ratio of hexane to oil, with no added silica. This bath was used to coat samples in a similar manner to the method described above, resulting in oil-coated fabrics without silica. A list of all the samples made is shown in table 2. The average net mass addition for each type of fabric for STF treated samples is shown in figure 3.

Table 2. Samples prepared for flammability testing.

Sample name	Fabric material	Treatment	Sample orientation	Percent mass addition	Number of samples
K706-W	K706	Neat	Warp	-	5
K706-F	K706	Neat	Fill	-	5
K706-Oil-W	K706	Oil	Warp	11.4%	2
K706-Oil-F	K706	Oil	Fill	8.1%	3
K706-STF-W	K706	STF	Warp	22.2%	4
K706-STF-F	K706	STF	Fill	20.8%	5
ACU-W	ACU	Neat	Warp	-	5
ACU-F	ACU	Neat	Fill	-	5
ACU-STF-W	ACU	STF	Warp	32.9%	3
ACU-STF-F	ACU	STF	Fill	39.5%	4
Felt	ArmorFelt	Neat	N/A	-	5
Felt-STF	ArmorFelt	STF	N/A	375%	1

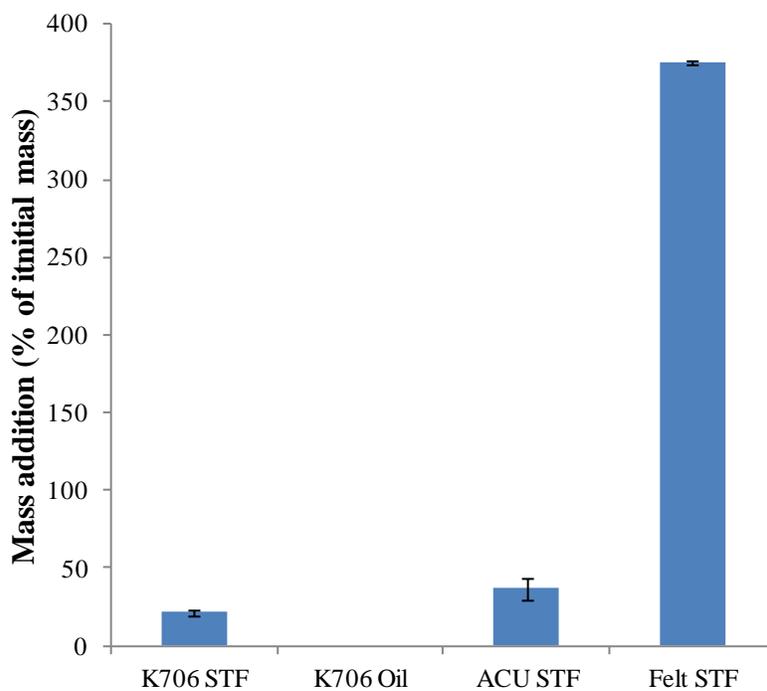


Figure 3. Net mass addition of oil and STF (percent of initial mass of fabric).

2.2.2 Vertical Flame Resistance Test

Flame resistance was quantified by metrics of afterflame time, afterglow time, and char length. To conduct a vertical flame resistance test, samples were mounted in a fixture that suspends the samples vertically, 19 mm above a Bunsen burner (see ASTM D4613 for mounting fixture details). The Bunsen burner flame was adjusted so that it was a consistent height (38 mm) for all samples. To eliminate the effects of drafts, a box (with two open faces) with dimensions 645 × 645 × 464 mm was placed around the sample testing area. Samples were exposed to the flame for 12 s and then the flame was moved so it was not in contact with the sample. After removing the flame, afterflame and afterglow times were measured.

Fabric char length was measured according to ASTM D6413 (figure 4). To measure char length, a crease was created in the specimen through the peak of the charred area and parallel to the sides of the specimen. A 100-g weight was attached to the bottom right corner of the fabric (6 mm from each side) using a hook. The side opposite of the hook was then lifted in a continuous motion until the tearing force is only supported by the sample. The end of the tear was marked with a line across the width of the sample and then the char length was measured along the undamaged edge of the specimen.

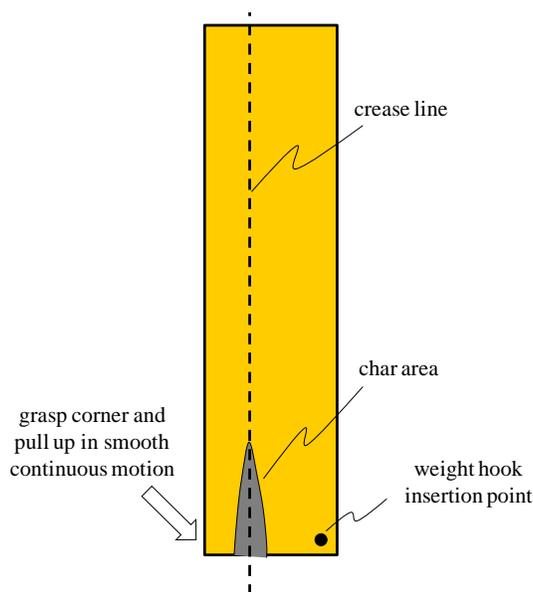


Figure 4. Char length measurement after vertical flame test.

2.2.3 Flash point measurements

In addition to measuring the flammability of STF treated fabrics, the inherent flammability of STF was evaluated through measurements made using the Cleveland Open Cup method (ASTM D92-05). Test samples were prepared by filling 70 mL of fluid into a 70-mm-diameter × 34-mm-high (inner dimensions) brass cup, which conforms to the dimensions listed in ASTM D92-05. The

brass flash cup was placed in an apparatus similar to ASTM D92-05, consisting of a hot plate, thermometer, and test flame applicator on swivel (figure 5). A photograph of the setup used to perform open cup measurements is shown in figure 6.

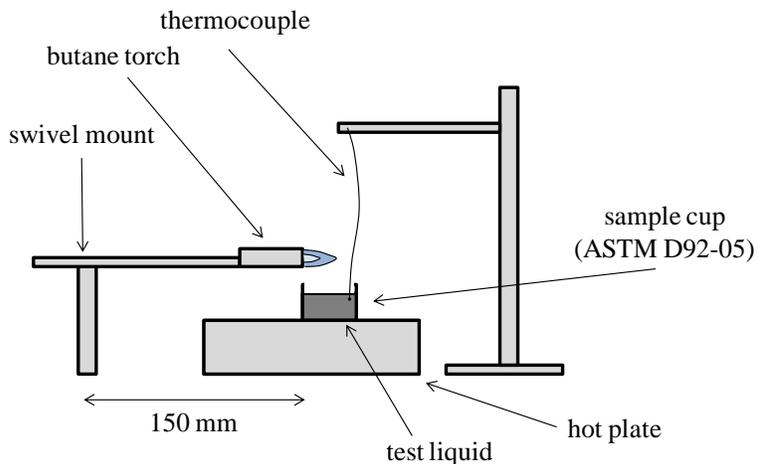


Figure 5. Schematic of setup used for flash point testing.

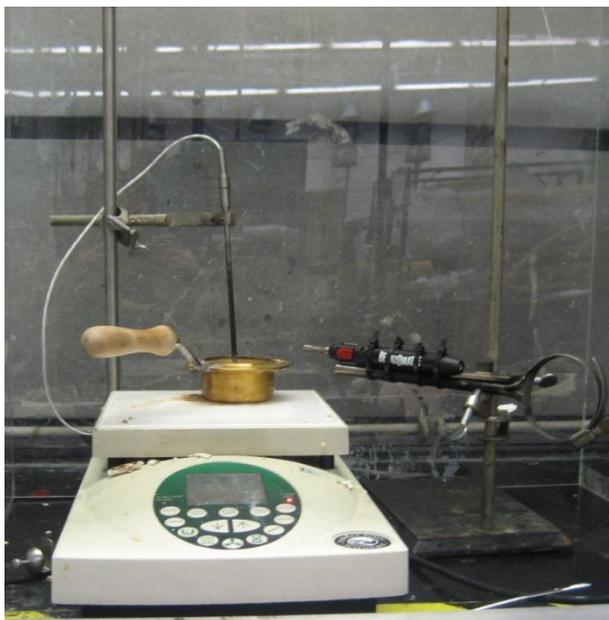


Figure 6. Experimental setup for flash point measurements.

Flash point measurements were conducted by igniting the test flame and adjusting the flame cone to a diameter of 3.2–4.8 mm (1/8 to 3/16 in.). The hot plate was then used to heat the flash cup at a rate of 5 to 6 °C/min until the measured temperature of the fluid was 28 °C below the estimated flash point.

When the temperature is 28 °C below the expected flash point, the test flame was applied to the vapors above the test cup for 1 ± 0.1 s by passing the flame in a horizontal plane 2 mm above the cup along the circumference of a circle having a radius of 150 ± 1 mm. The test flame was swung in a continuous fashion so that the rate of application of heat would be constant between tests. The flame was reapplied to the sample in the same fashion every 2 °C until the flash point was obtained, based on visual observation of flame ignition above the cup. After obtaining the flash point, a fresh sample was loaded and the test was repeated starting a temperature 28 °C below the flash point detected on the first test.

3. Results

3.1 Neat K706 Warp versus Fill

Figure 7 shows photographs comparing the vertical flame resistance of K706 oriented in the warp versus fill direction (K706-W versus K706-F). The amount of char generated through this test on plain Kevlar is very small, between 6–10 mm. No afterflame was observed on neat Kevlar, only an afterglow. There is little systematic difference in char length or character between the warp and fill directions. Based on this result, all subsequent experiments using warp-oriented and fill-oriented test samples are averaged and reported together.

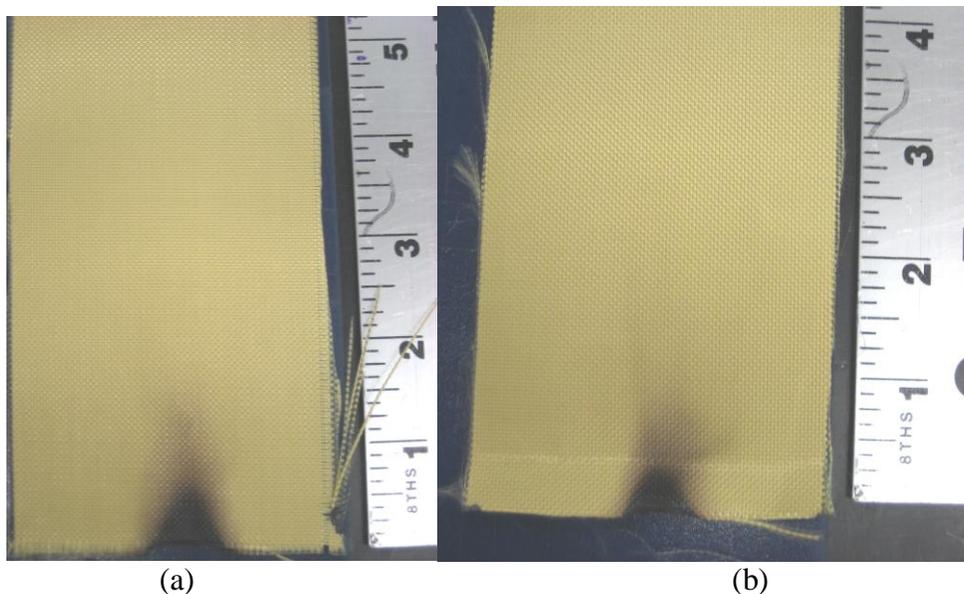


Figure 7. Post-test images of (a) warp-oriented, neat K706 (K706-W) and (b) fill-oriented, neat K706 (K706-F).

3.2 Neat K706 versus Oil-Treated K706

Oil-treated Kevlar and neat Kevlar are compared in figure 8, for the warp direction. A larger charred area and a longer afterglow time were observed in oil-treated samples compared to neat samples. Oil-treated Kevlar did not show an afterflame.

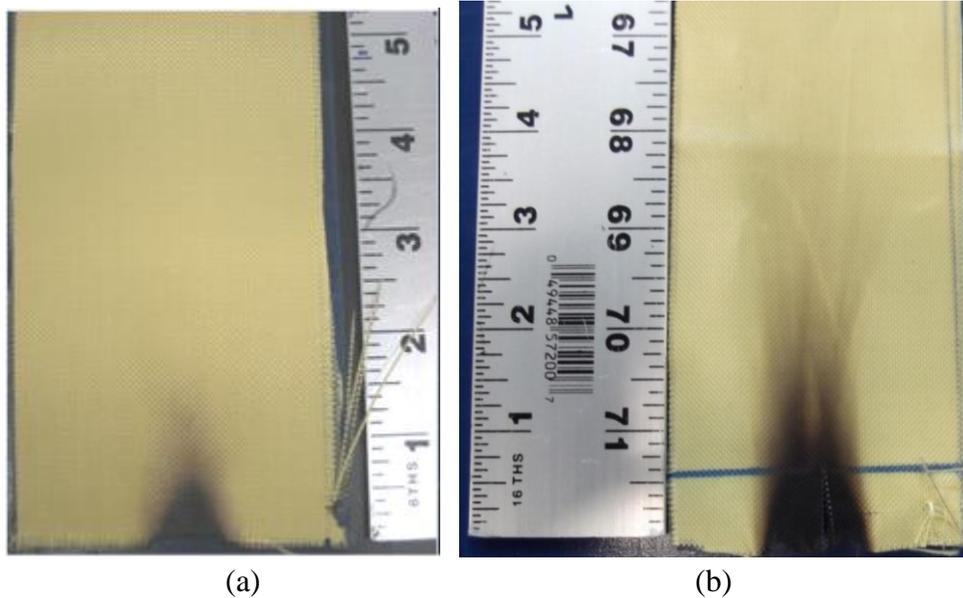


Figure 8. Post-test images of (a) neat K706 (K706-W) and (b) oil-treated K706 (K706-Oil-W).

3.3 Neat K706 versus STF-treated K706

Figure 9 shows a comparison between plain Kevlar and STF-treated Kevlar, both oriented in the warp direction ([a] Plain-W4 [b] STF-W3). The STF-treated Kevlar shows a smaller amount of black char when compared to plain Kevlar. In addition to black char, a white char appeared on the STF treated Kevlar, most likely silica residue from the STF. Only a small amount of black char is visible on sample STF-W3, which indicates that the fabric was less damaged by the vertical flame resistance tests compared to neat Kevlar. During the tests, STF-treated fabrics did not show an afterflame and only a shorter afterglow than Plain-K706 or Oil-K706.

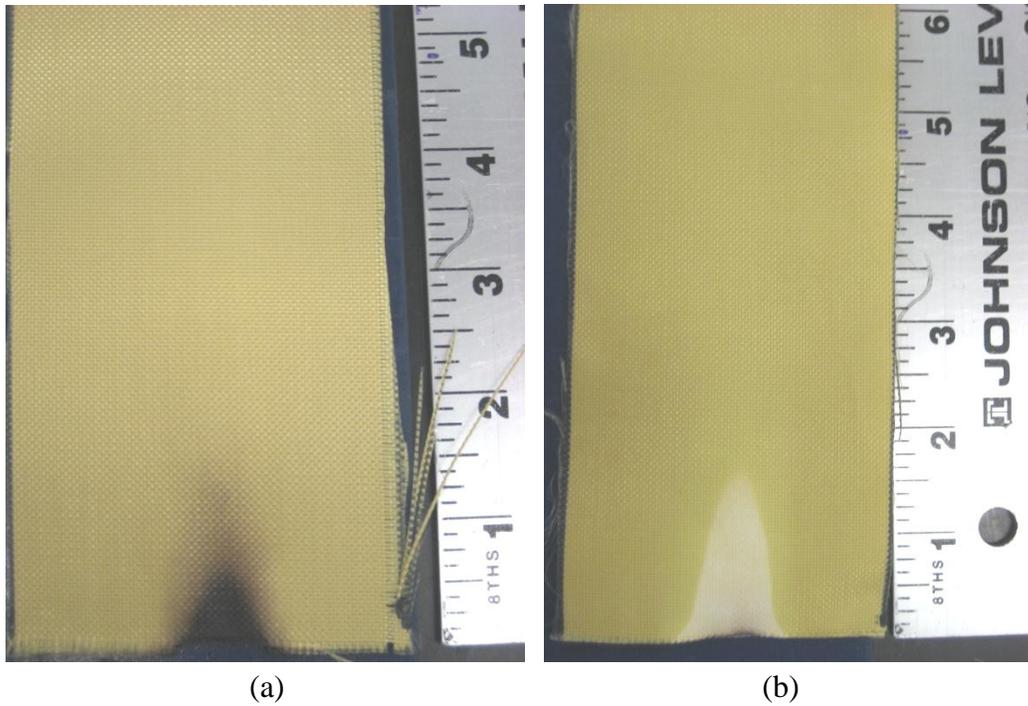


Figure 9. Post-test images of (a) neat K706 (K706-W) and (b) STF-treated K706 (K706-STF-W).

3.4 Neat ACU versus STF-treated ACU

Figure 10 shows flammability testing of neat ACU fabric. ACU fabric ignited easily and was engulfed in flames after 12 s of flame exposure. Char propagated approximately 140 mm after 12 s of flame time (figure 10 [b]). After removal of the test flame the flame propagated quickly up the fabric and was extinguished after the entire fabric was covered in char. Like the Kevlar samples, no differences in flammability for warp and weft orientation samples were observed, therefore all data is averaged and reported together regardless of orientation.

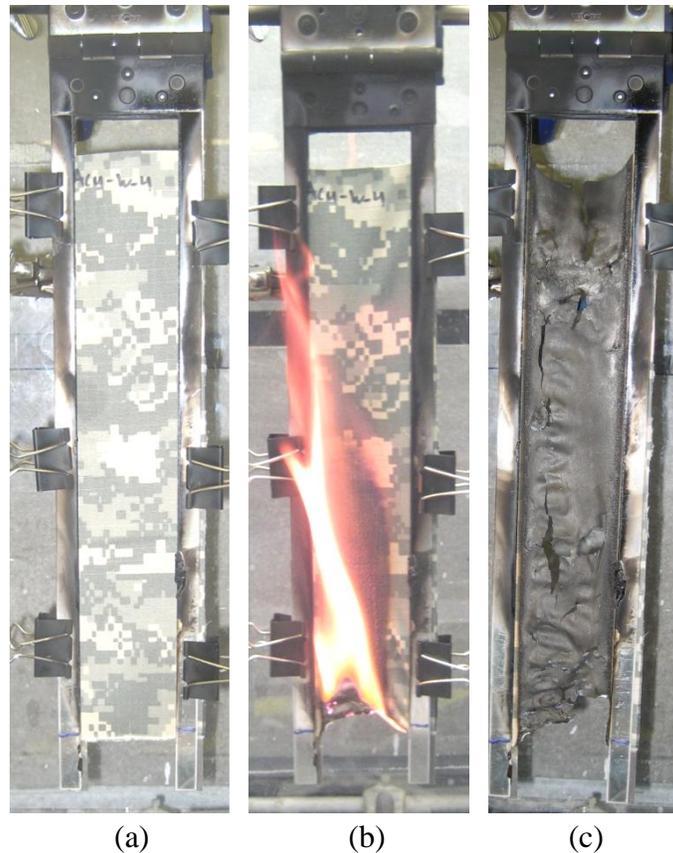


Figure 10. Flammability testing of neat ACU fabric (ACU-W) at (a) 0 s, (b) 12 s, and (c) test completion.

Figure 11 shows flammability testing of STF-treated ACU. STF-treated ACU fabric showed slower ignition than neat ACU fabric. Fabric ignited after 11 s of application of the test flame and the char propagated approximately 70 mm after 12 s application of test flame. During the propagation of the flame, a white surface layer formed on the fabric, starting from the edge where the test flame was applied and continuing to form as the flame traveled along the fabric strip (figure 11 [b]). Flame propagation continued until the entire fabric was consumed. After the fabric was consumed no afterglow was observed. The final char length was measured as the entire length of the fabric strip. Comparing figures 10 (b) and 11 (b), the rate of flame propagation (speed at which the char front travelled along fabric, not the flame height) for the STF-treated ACU is considerably slower than the rate observed for the neat ACU fabric.

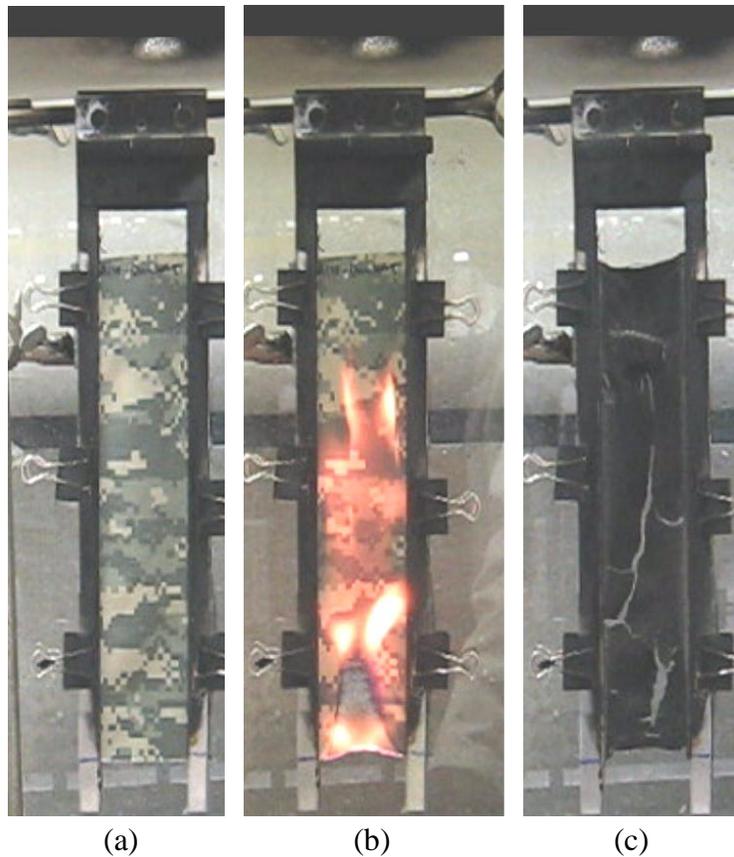


Figure 11. Flammability testing of STF-treated ACU fabric (ACU-STF-W) at (a) 0 s, (b) 12 s, and (c) test completion.

3.5 Neat Armorfelt versus STF-treated ArmorFelt

The Armorfelt and STF-treated ArmorFelt had similar behaviors when subjected to the vertical flammability test. Both fabrics ignited slowly, approximately 11 s after the fabrics' initial exposure to the test flame. After the fabric's ignition, the flame propagated slowly up the fabric, while giving off white smoke and a waxy odor (consistent with burning behavior of UHMWPE). After the flame propagated approximately three-fourths of the way up the fabric the smoke changed from white to brown in color. The flame was self-extinguished after reaching the top of the fabric and no afterglow was observed. Figure 12 shows a comparison between plain ArmorFelt and STF-treated ArmorFelt after testing. Samples are nearly indistinguishable; however, the STF treated ArmorFelt fabric shows a concentration of char at both the top and bottom of the fabric, while the plain ArmorFelt shows a mostly uniform char pattern. Char length measurements indicated that that the felt was still mechanically intact after testing, suggesting that the UHMWPE fibers, rather than the Kevlar fibers, burned during the experiment.

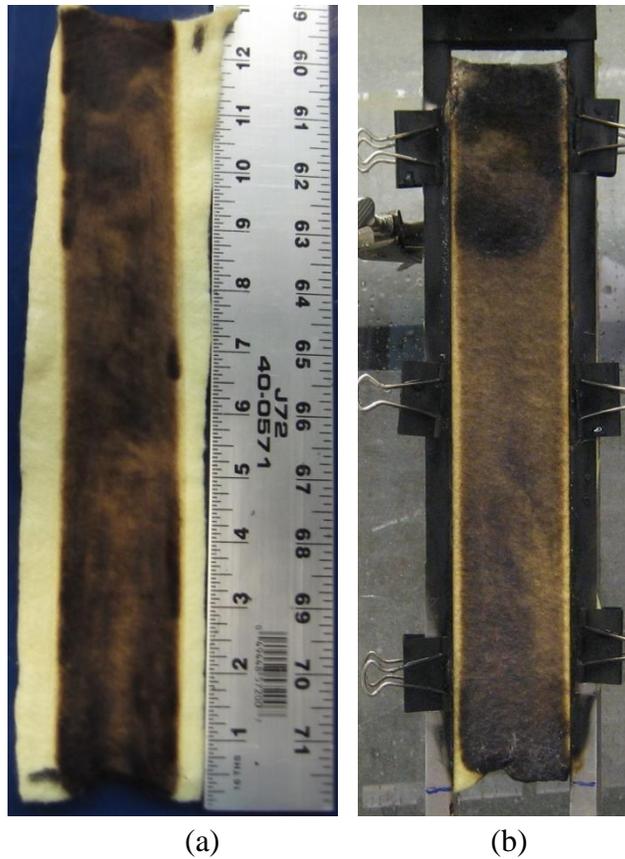


Figure 12. Post-test images of (a) neat felt and (b) STF-felt.

3.6 Summary Data

Figure 13 compares average afterflame time for the different samples, with the standard deviation of the results represented by the error bar. As described in the Introduction, zero afterflame time is most desirable, indicating that the material did not readily burn. However, if the material does burn, it is desirable to have a longer afterflame time, which is indicative of a slow-moving flame and a material that does not readily burn. For the K706 samples, fabrics did not display an afterflame so the afterflame time is recorded as zero. Plain ACU displayed an afterflame time between 34–39 s, while STF-ACU displayed an afterflame time between 40–50 s. This result indicates that flame propagation was slower with the STF-ACU sample. Note that both ACU fabrics did not self-extinguish until the flame had consumed all of the fabric. Plain ArmorFelt fabric displayed the longest afterflame time out of all of the plain fabrics. STF treatment of the ArmorFelt fabric nearly doubled the afterflame time. It should be noted that the ArmorFelt fabric also absorbed the greatest amount of STF out of all of the fabrics (375% of initial mass).

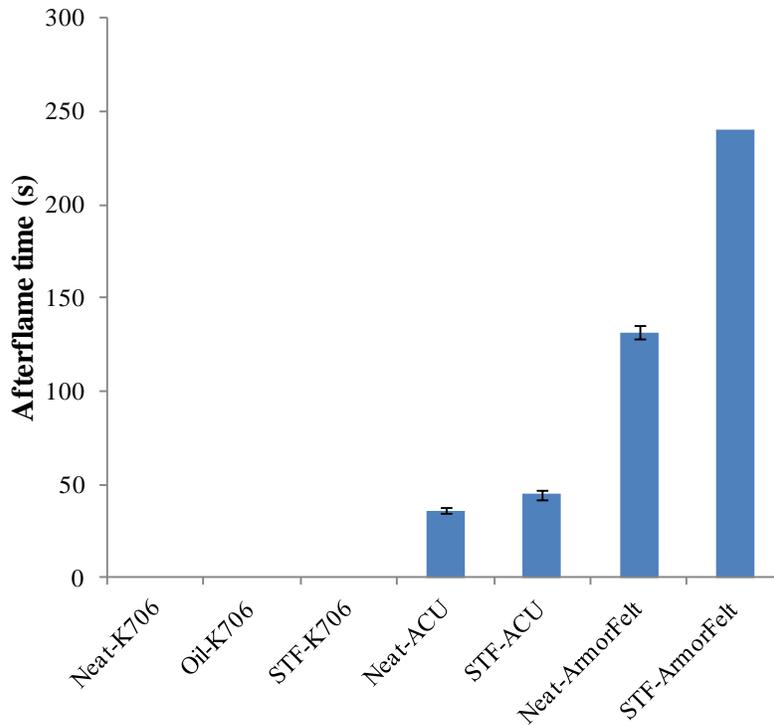


Figure 13. Comparison of afterflame time for tested fabrics.

The average of the afterglow time for different fabric samples are compared in figure 14, with the error bar representing the standard deviation of the results. A short afterglow time is preferred, indicating that the material readily self-extinguishes. Zero afterglow is noted for the ACU and felt samples, as the flammable material components were apparently fully consumed during flame propagation. All K706 samples showed an afterglow. The oil-treated K706 showed a statistically significant increase in afterglow time from plain K706. The STF-treated K706 showed a statistically significant decrease in afterglow time from both K706 and oil-treated K706.

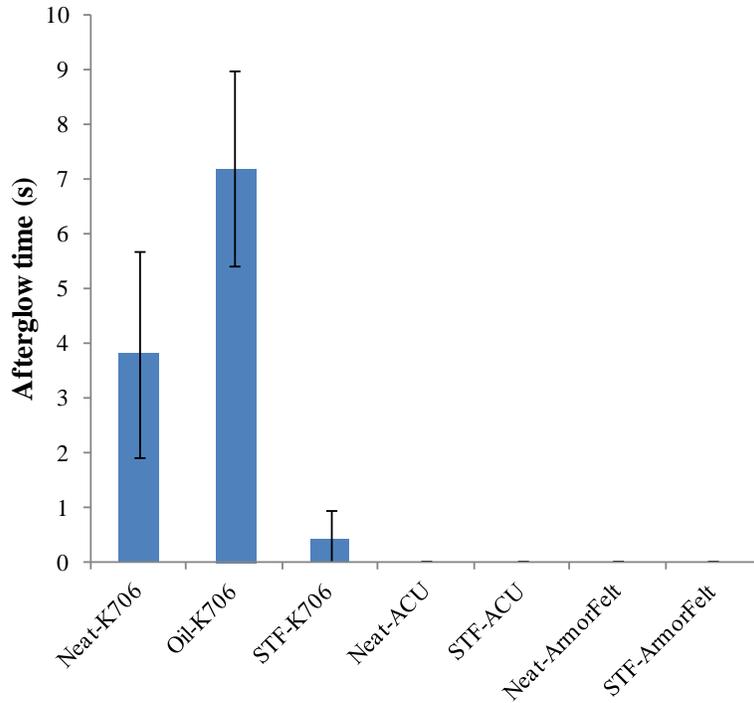


Figure 14. Comparison of afterglow time for tested fabrics.

Figure 15 shows a comparison of the the char length for the tested fabrics on a log scale. A shorter char length indicates that the mechanical properties of the fabric were better preserved after exposure to flame. Overall, ACU fabrics showed the longest char length, and Armorfelt fabrics showed the shortest. The STF treatment had an insignificant effect on the length of char on all samples except for K706, where a slight reduction was observed.

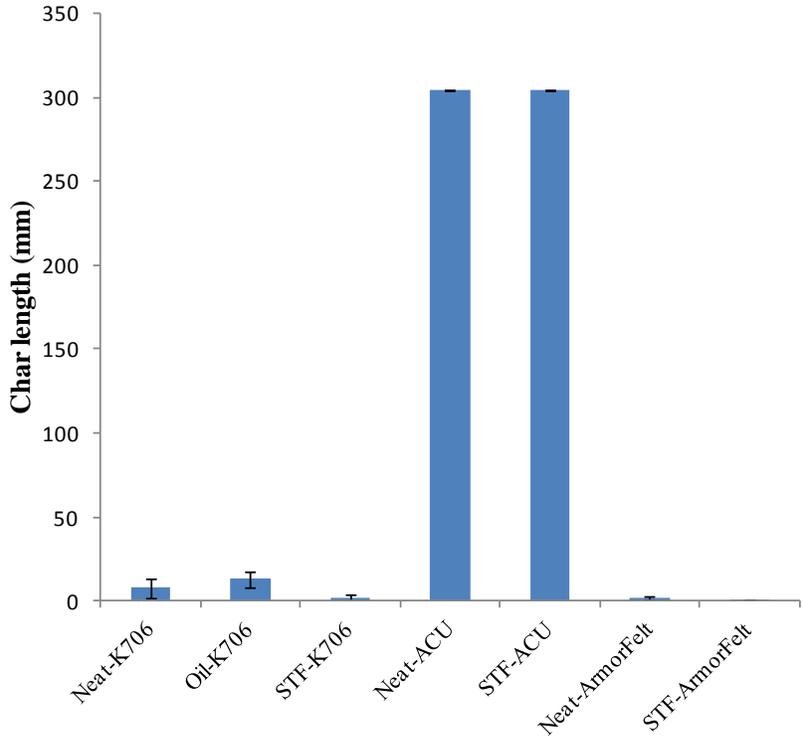


Figure 15. Comparison of char length for tested fabrics.

Minimal differences were observed in afterglow and char length measurements between warp-oriented and fill-oriented neat K706 samples. Similarly, no statistical difference was observed between warp-oriented and fill-oriented neat ACU samples. Comparing neat, oil-treated, and STF-treated K706 samples (figure 16), some orientation differences are noted but no consistent trends persist across different fabric treatments.

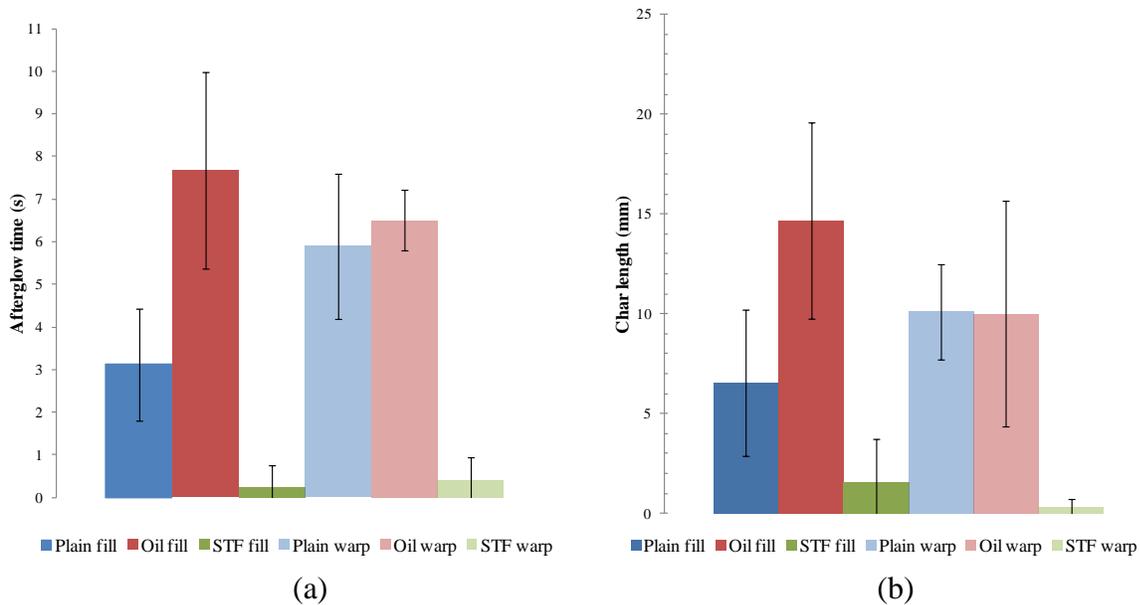


Figure 16. Comparison of warp-oriented vs. weft-oriented K706 fabric, (a) afterglow time and (b) char length.

3.7 STF Flash Point

The flash point of the neat paraffin oil was measured to be ± 1 °C within 229 °C, consistent with manufacturer-provided values and providing validation of the test method. The flash point for the oil-based STF was found to be 164 °C, which is substantially lower than the flash point of oil alone. However, the STF was observed to form a surface foam (shown in figure 17), which ignited at a core temperature of 164 °C when the foam reached a sufficient height to be directly ignited by the test flame. In contrast, for the neat oil only vapors were emitted above the test cup surface and the oil itself did not make contact with the flame. Therefore, the lower flame point value for the STF samples is somewhat misleading. The foam is likely generated by higher volatility solvents boiling within the oil, with the silica nanoparticles acting like a physical surfactant that stabilizes the bubble walls (a “Pickering foam” [14]).

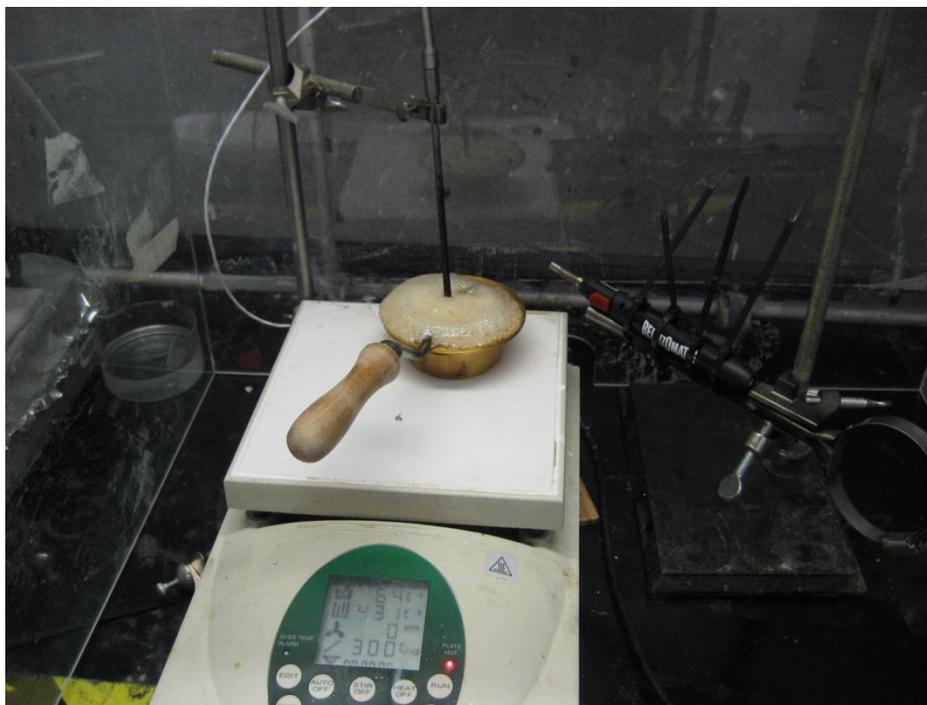


Figure 17. STF flash point experiment. Note the foam rising above the sample cup.

4. Discussion and Conclusions

4.1 Influence of Fabric Material

Considering the neat textiles, K706 showed the best flame-resistance (by metrics of smallest char length, shortest afterglow). The worst flame-resistant material was determined to be ACU (nylon/cotton blend), which displayed the shortest afterflame time and had a char length equal to the entire length of the fabric. These results are not surprising as textile fabric flammability

commonly correlates with thermal degradation temperature of the constructing polymer (15). Based upon thermal degradation temperatures (table 3 [16]), it would be expected that ACU (nylon/cotton) would be the most flammable followed by the Armorfelt (PE/para-aramid blend), followed by pure Kevlar. Since the thermal degradation temperature of polyethylene is so much lower than that of Kevlar, one would expect that a pure Kevlar felt would exhibit significantly less flammability than the polyethylene/Kevlar blend in the ArmorFelt material.

Table 3. Thermal degradation temperatures of selected materials

Material	Thermal degradation temperature (°C)
Kevlar	400
Nylon-6	310
Polyethylene	149
Cotton	106

4.2 Influence of STF Treatment

The STF treatment addition had a minor to moderate effect on fabric flammability. For K706, STF treatment led to decreased afterglow time and char length, indicators of flame retardancy. For the ACU fabric, the rate of flame propagation in the STF-treated sample appeared to be somewhat slower compared to the neat sample, but all other flammability metrics showed no clear differences. For the ArmorFelt, STF addition increased afterflame time significantly, while decreasing char length slightly, suggesting some flame retardancy. In comparison, the oil-treated K706 samples showed higher afterglow time compared to neat K706, suggesting a slight increase in flammability. Overall, these results indicate that the addition of an STF does not increase fabric flammability, and in fact may decrease flammability slightly. This important conclusion demonstrates that oil-based STFs can be used for textile treatments without creating unacceptable changes to the flammability of the textile.

4.3 Designing an STF Treatment for Flame Retardancy

The STF characterized in this study was formulated for a particular rheological response and consistency, without consideration of flame retardancy. It is possible that one could design an STF specifically with the intent to increase flame retardancy, creating a multifunctional coating that enhances the fabric mechanical properties (such as puncture and ballistics) while also providing enhanced flammability, perhaps even replacing existing flame resistant coatings such as those used on newer flame-resistant ACUs.

The moderate flame retardancy noted for the STF used in this study is most likely caused by the silica particles, which create a ceramic barrier on the textile surface which impedes the transport heat and oxygen to the polymer surface. This flame retardancy approach has been previously

reported for fillers including silica (12, 13), aluminum hydroxide (17), and montmorillonite (17). Beyond these passive fillers, one could also imagine fillers that actively react or decompose to assist with flame retardancy. For example, under high heat, a calcium carbonate particle would undergo an endothermic decomposition, absorbing 178 kJ/mol of heat, while releasing CO₂ that would dilute the concentration of fuel and oxygen in the vapor phase according to:



Calcium carbonate is available in colloidal form, and multiple studies have shown that it can be formed into a shear thickening fluid that can be added to textiles to enhance low velocity ballistic performance (18).

Similarly, the liquid phase of the STF could be selected to provide flame retardancy. Silicone oils and fluorinated oils are known to be non-flammable. Other flame retardant additives such as an organohalogen or organophosphorus could also be directly integrated into the host fluid.

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